Studies of ion bombardment in high density plasmas containing CF$_4$

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We report ion energy distributions, relative ion intensities, and absolute total ion current densities at the grounded electrode of an inductively coupled Gaseous Electronics Conference radio-frequency reference cell for discharges generated in pure CF$_4$, and in CF$_4$:Ar and CF$_4$:O$_2$:Ar mixtures. Abundant ionic species, including secondary ions such as CO$^+$ and COF$^+$, were observed and their implications are discussed.   [S0734-2101(99)03204-2]

I. INTRODUCTION

Carbon tetrafluoride (CF$_4$) is a commonly used gas for the plasma etching of Si and SiO$_2$ surfaces,[1] and for plasma chamber cleaning processes when mixed with oxygen.[2] To efficiently perform these functions, a high-density, low-pressure plasma source that produces a significant ion flux is required.[3] While the production of neutral and radical species in CF$_4$, high-density, inductively coupled plasmas has been studied in significant detail,[4–6] there is little known concerning the composition, magnitude, and energy of the ion flux striking the surfaces exposed to these discharges. Several studies have been performed related to the ion flux generated in low-density CF$_4$ plasmas,[7–9] but only one study has been published for a high density source.[10]

In this article we present mass analyzed ion-energy distributions (IEDs) and ion flux densities measured by a combined ion energy analyzer-mass spectrometer that samples plasma ions through an orifice in the lower electrode of a high-density, inductively coupled Gaseous Electronics Conference (GEC) radio-frequency (rf) reactor. Data are presented for plasmas generated in pure CF$_4$, and in mixtures of CF$_4$ with argon and oxygen. It is shown for these high-density plasmas containing CF$_4$ that mass analysis of the ion flux is essential since many ions exhibit significant abundances. This is unlike many low density, capacitively coupled, CF$_4$ plasmas where the CF$_3^+$ ion often accounts for the vast preponderance of the ion flux.

II. EXPERIMENT

Plasmas were generated in a GEC rf reference reactor[11,12] whose upper electrode was modified to house a five-turn planar rf-induction coil behind a quartz window to produce inductively coupled discharges.[13] The reactor, along with the ion-energy analyzer and mass spectrometer, are shown schematically in Fig. 1. The feed gas enters the cell through one of the 2.75 in. side flanges and is pumped out through the 6 in. port attached to the turbomolecular pump. The gas pressure is maintained by a variable gate valve between the

pump and the GEC cell. The flow was maintained by mass flow controllers at 7.45 μmole/s (10 sccm) for all of the experiments reported here.

The discharge is generated by applying a 13.56 MHz voltage to the coil in the upper electrode through a matching network. The rf power values presented in this article are the net power to the matching network driving the coil. The actual rf power dissipated in the plasma has been determined to be approximately 80% of the power listed.[13] The lower electrode was grounded to the vacuum chamber.

The ion sampling arrangement is the same as that used to study inductively coupled plasmas generated in Ar, N$_2$, O$_2$, and Cl$_2$.[14] Ions are sampled through a 10 μm diam orifice in a 2.5 μm thick nickel foil that was spot welded into a small counter bore in the center of the stainless steel lower electrode. The mass spectrometer with ion energy analyzer used here is the same instrument used to measure ion-energy distributions in a capacitively coupled GEC rf reactor[15] and in high pressure dc Townsend discharges.[16] For IED measurements, the ions that pass through the orifice are accelerated and focused into a 45° electrostatic energy selector. After being selected according to their energy, the ions enter a quadrupole rf mass filter where they are also selected according to their mass-to-charge ratio (m/z). The resolution of the electrostatic analyzer was fixed at a value of 1 eV, full width at half maximum, and the uncertainty in the energy scale is estimated to be ± 1.0 eV.

Past experience with the ion-energy analyzer[16] indicates that the ion transmission is uniform over the ion energy ranges observed here. The mass spectrometer was tuned such that the ion transmission was nearly constant over the range of ion masses detected here (12–80 u), however, a transmission correction factor[14] was applied to the highest mass ions (mass >40 u) to compensate for some decrease in ion transmission with increasing mass.

For total ion current measurements (i.e., all ion current passing through the sampling orifice), the ion optic elements at the front of the ion-energy analyzer were biased such that the current passing through the sampling orifice was collected on the extractor element (the first ion optic element behind the electrode surface), and was measured by an electrometer. The total ion current (flux) measurements exhibited a scatter of $\pm 20\%$ for plasmas with the same pressure,

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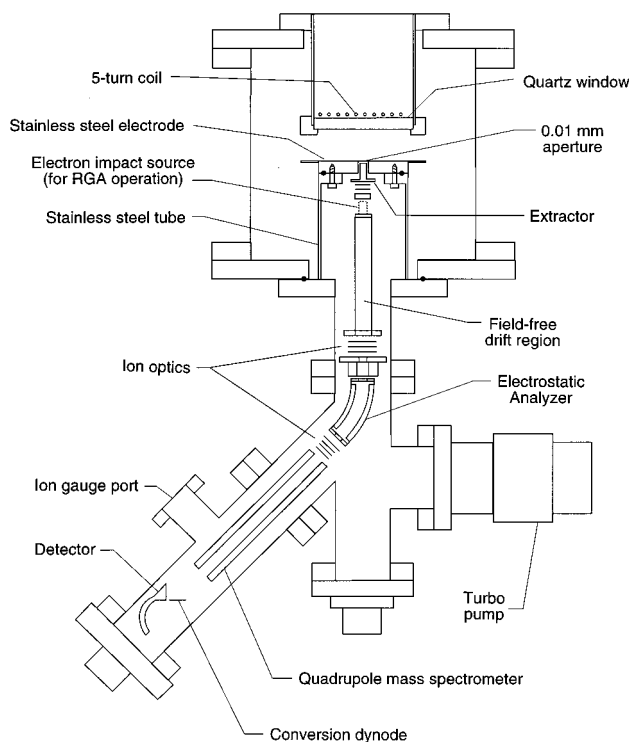b)Electronic mail: yicheng.wang@nist.gov

FIG. 1. Schematic diagram of the inductively coupled GEC rf reference reactor with the ion-energy analyzer and mass spectrometer appended to the modified lower electrode.

FIG. 2. (a) Mass spectrum of ions striking the lower electrode in the GEC cell from a 200 W, 1.33 Pa, CF_4 discharge. (b) Ion energy distributions of the five dominant ions produced in the CF_4 plasma. The absolute flux density of individual ion species was obtained by normalizing the total counts of the mass scan to the total current measured through the 10 μm orifice.

power, and gas composition, most likely due to changes in surface conditions near the sampling orifice. The absolute intensities of the measured IEDs were scaled to the measured values of the total ion current. The ion flux densities presented here were determined by dividing the total measured ion current by the area of the 10 μm diam sampling hole. The diameter of the sampling orifice was verified by observation under a high powered microscope, and was determined to be within $\pm5\%$ of the stated diameter.

III. RESULTS AND DISCUSSION

A. Pure CF$_4$

Figure 2(a) shows a mass spectrum of the ions produced in a pure CF_4 plasma at 1.33 Pa (10 mTorr) and 200 W that strike the grounded electrode. CF_3^+ is the dominant ion, but a significant contribution is observed from CF_2^+ and CF^+ (CF_4^+ is unstable). These ions are expected to result primarily from direct electron-impact ionization of CF_4, which is consistent with a low degree of dissociation of the CF_4 feed gas under these conditions.[17] Secondary ions, particularly O-containing ions, resulting from ion-molecule or ion-surface interactions are also present in the plasma. The secondary ion exhibiting the largest ion flux is observed to be CO^+, which has an intensity comparable to CF_2^+. Possible sources of the oxygen are from water desorbed from the interior surfaces of the reactor and O liberated from the oxide-covered metallic electrode or quartz window surfaces. The fact that oxygen-containing ions are a significant com-
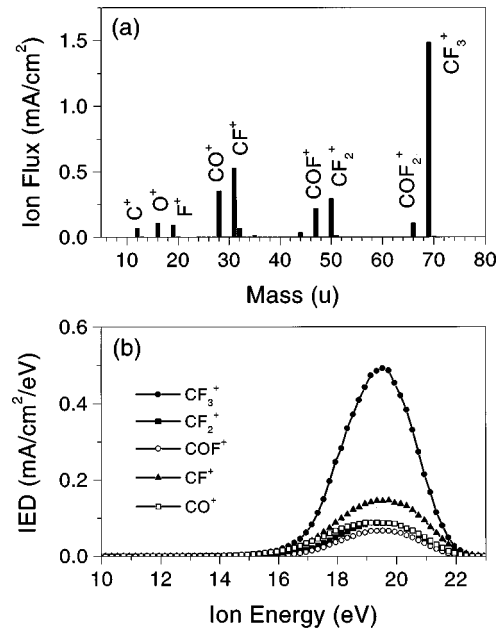
ponent of the ion flux is significant for industrial reactors which always contain a substantial amount of water (due to the introduction of wafers into the chamber) and oxidized aluminum surfaces.

While CF_3^+ is the dominant ion observed in this CF_4 plasma, the four next most abundant ions exhibit intensities with magnitudes of approximately 20% of the intensity of CF_3^+. This is in contrast to previous studies of ions produced in low-density, CF_4 plasmas in capacitively coupled reactors,[7–9] where CF_3^+ is often the dominant ion by a factor of 10 or more. For the plasma studied here, CF_3^+ accounts for barely half of the total ion flux.

The IEDs of the five most abundant ions seen in Fig. 2(a) are presented in Fig. 2(b). All IEDs display a single narrow peak, with approximately the same width and peak position, indicating that all ions originate from the bulk plasma. These IEDs are similar to those measured from high density plasmas in argon.[14]

The plasma potentials, which correspond to the mean energies of the measured IEDs, are shown in Fig. 3 as a function of pressure for discharges in pure Ar, CF_4, and a 50% CF_4 : 50% Ar volume mixture at 200 W. For all three cases, the plasma potential decreases with increasing pressure, indicating lower electron energies at higher discharge pressures. The plasma potential for pure CF_4 is higher than that for Ar by about 2.5 eV at all pressures, indicating higher mean electron energies in CF_4, consistent with previous observations of higher electron energies in plasmas containing electronegative gases.[18] This effect is significantly reduced in the CF_4:Ar mixture where the plasma potentials are nearly identical to those measured in argon.
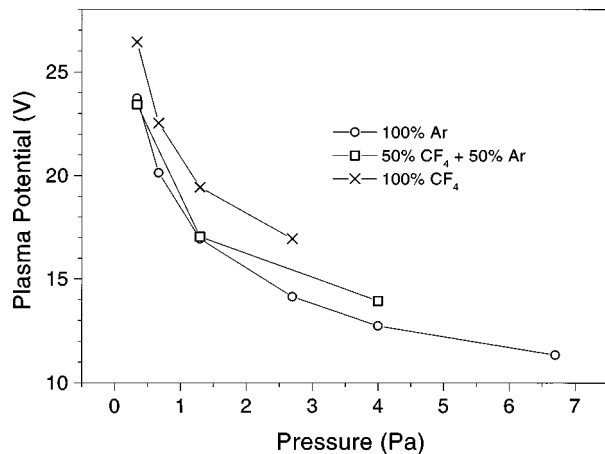
FIG. 3. Plasma potentials, determined from the mean energies of the measured IEDs, as a function of pressure for plasmas generated in pure argon ($\bigcirc$), pure CF_4 ($\times$), and a 50/50 mixture ($\square$).

B. CF_4:Ar mixture

Figure 4(a) shows the total ion flux and the fluxes of component ions for an inductively coupled plasma sustained in a 50% CF_4:50% Ar volume mixture at 200 W as a function of gas pressure. The magnitude of the total ion flux exhibits a slight downward trend as the pressure increases above 0.67 Pa (5 mTorr), in contrast to that observed in pure Ar and in mixtures of argon with O_2 and Cl_2.[14] The dominant ion detected from the mixture is Ar^+ at the lowest pressure and is CF_3^+ at higher pressures. The decreasing Ar^+ flux and corresponding increase in CF_3^+ flux with increasing pressure may be partly due to the dissociative charge transfer reaction involving Ar^+ and CF_4. The cross section for this reaction is large at ion energies common to the glow region of the discharge ($\sim 100 \times 10^{-20}$ m^2 at 0.1 eV).[19]
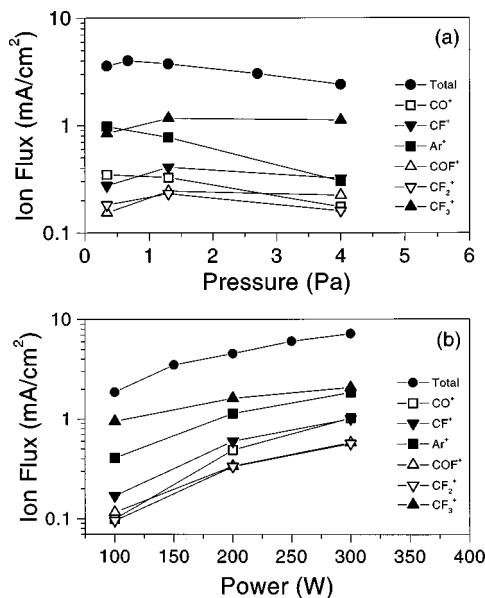

FIG. 4. Mass analyzed ion flux striking the lower electrode measured for a plasma in a 50%Ar:50%CF_4 mixture (a) as a function of pressure and (b) as a function of power.
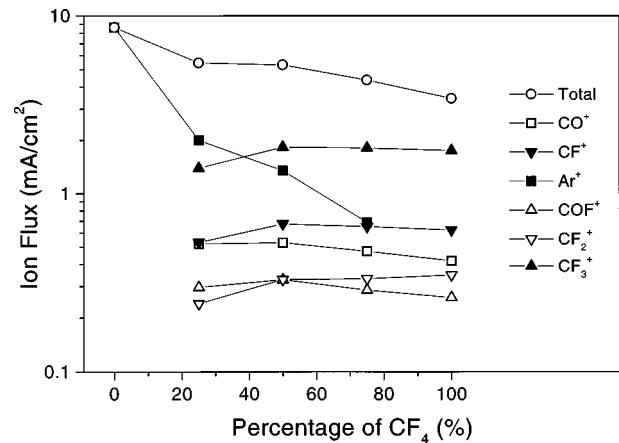

FIG. 5. Mass analyzed ion flux striking the lower electrode of 200 W CF_4:Ar plasmas at 1.3 Pa as a function of gas composition.

The total ion flux and fluxes of the component ions are shown in Fig. 4(b) as a function of plasma input power for the same mixture at 1.3 Pa. The total ion flux and the fluxes of component ions all increase with increasing input power from 100 to 300 W. While the CF_3^+ flux dominates at 100 W, the intensities of Ar^+ and CF_3^+ are comparable at 300 W. It is interesting to note that the CF_3^+ flux increases at a slower pace with power than the total ion flux, while the flux of the secondary CO^+ ions increases more rapidly than the total flux.

Figure 5 shows the total ion flux and the fluxes of component ions in a CF_4:Ar mixture as a function of the percentage of CF_4 in the mixture by volume at 1.3 Pa and 200 W. The total ion flux decreases when CF_4 is added to the pure Ar plasma and continues to decrease as the percentage of CF_4 in the mixture increases. This general decrease can be attributed to the decreasing plasma density due to increasing electron attachment to CF_4. It is interesting to note that the Ar^+ ion flux decreases by a factor of 3 from 25% CF_4 to 75% CF_4 in the mixture, approximating the net decrease of the neutral argon concentration in the plasma. However, the fluxes of all ions originating from CF_4 exhibit little change in absolute or relative intensities as the CF_4 percentage increases from 25% to 100%. This observation may have implications in optimizing reactive plasmas as the reactive ion species cannot be readily increased by increasing the concentration of CF_4 in the plasma.

The ion-energy distributions of Ar^+, CF_3^+, CF_2^+, and CF^+ obtained under the same conditions as in Fig. 5 are shown in Fig. 6. As can be seen in Fig. 6, the IEDs for CF_3^+, CF_2^+, and CF^+ are similar and vary little in shape as the CF_4 percentage changes. The plasma potential, as exhibited by the energies corresponding to the peaks of the IEDs, increases with increasing percentage of CF_4, again indicating that the mean electron energies increase as more electron attaching gas is introduced into the plasma.

C. CF_4:O_2:Ar mixture

Figure 7 shows the total ion flux and the fluxes of component ions measured in an 80% CF_4:10% O_2:10% Ar plasma
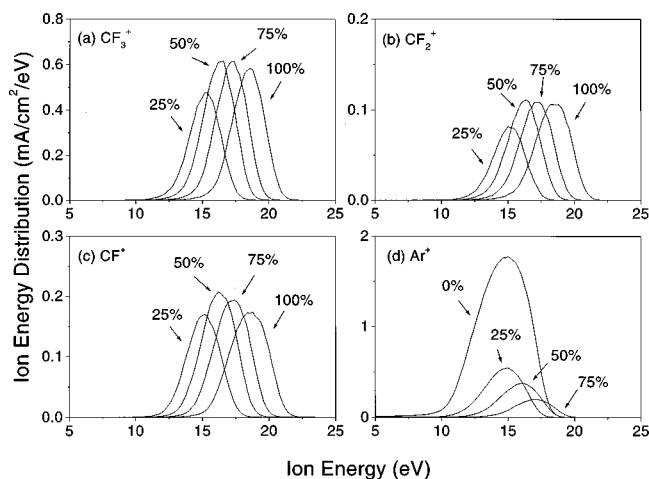
FIG. 6. Ion energy distributions for four significant ions sampled from 200 W, 1.3 Pa CF_4:Ar plasmas as a function of gas composition.

at 1.3 Pa (10 mTorr) and 300 W as a function of gas pressure. This gas mixture is similar to those used in plasma chamber cleaning applications.[2] While many cleaning processes are neutral driven, the flux of ions influences the cleaning rate. Figure 7, which shows 10 ionic species of significant intensities, amply demonstrates the complexity of ion-molecule or ion-surface interactions in a plasma involving gas mixtures. While CF_3^+ is obviously the dominant ion, the CF_3^+ ion flux accounts for less than one third of the total ion flux at all pressures for this gas mixture. This is different from the situation modeled by Ventzek et $al.$[20] for an inductively coupled plasma in a gas mixture containing a larger amount of argon (85%Ar:13%CF_4:2%O_2) where Ar^+ is clearly the dominant ion.

Interestingly, CO^+, which results from ion-molecule or ion-surface interactions, is the second-most dominant ion at all pressures. The fluxes of atomic ions including C^+, O^+,
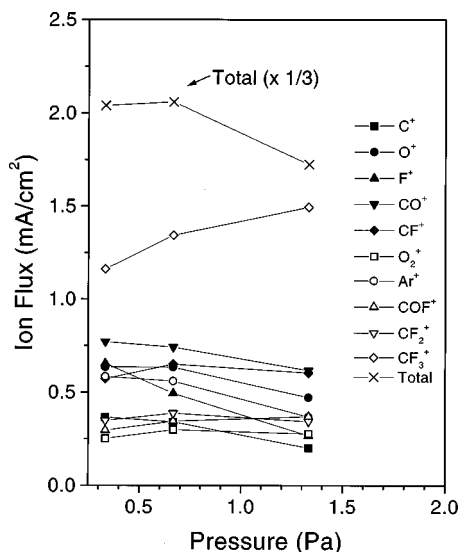
and F^+ are also considerably higher than those observed in pure CF_4 or CF_4:Ar mixtures. The flux of F^+ ions is observed to decrease by more than a factor of 2 as the discharge pressure increases from 0.34 to 1.3 Pa, although the total ion flux changes by less than 20% in the same range. This rapid drop of F^+ flux and the associated increase in CF_3^+ flux may be attributed to the fast charge transfer reaction involving F^+ and CF_4.[21] CF_3^+ is the only ion that shows a significant increase with increasing pressure.

IV. CONCLUSIONS

In general, the number of ionic species observed in the high density plasmas studied here significantly exceed those observed in low density plasmas generated in capacitively coupled reactors. Additionally, we have observed substantial fluxes of secondary ions, such as CO^+ and COF^+, resulting from reactions within the cell during CF_4 plasmas. These ions are of comparable intensity to some of the CF_x^+ ions that result from direct electron-impact, dissociative ionization of CF_4. In particular, 10 ionic species of significant intensity were observed in a CF_4:O_2:Ar plasma. An understanding of how these ions are produced, destroyed, and influence surface reactions is essential to fully understand and ultimately control these plasma processes.

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FIG. 7. Mass analyzed ion flux, as a function of pressure, in an 80%CF_4:10%O_2:10%Ar plasma at 300 W and 1.3 Pa.